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CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

NEW METHODS OF DETERMINING THE SPECIFIC HEAT AND THE REACTION-HEAT OF LIQUIDS.

By Theodore William Richards and Arthur Becket Lamb.

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Introduction.

The determination of the specific heats of solutions is a matter of importance, not only because these values are a necessary part of all thermochemical calculation, but also because of the probable connection between change of heat capacity and the "bound energy" of a reacting system.* Moreover, the irregular relations apparently existing between the values themselves still lack adequate explanation — and no satisfactory explanation can be given until the facts are more definitely and exactly known.

These considerations induced us to undertake the study of the problem, and the present paper recounts as briefly as possible the devices which were found to be necessary in order to eliminate the most serious possibilities of error.

The study of the heat capacity of liquids led directly, as will be seen, to a study of the heat of reaction evolved by mixing liquids; and for this purpose also new devices were found to be serviceable and conducive to precision. Because the two investigations are closely allied, they are given here together.

* Richards, These Proceedings, **38**, 293 (1902); Van't Hoff, Drude's Annalen, Boltzmann.

Previous Direct Methods of Measuring the Specific Heats of Salt Solutions.

The brief discussion of the methods which previous investigators have used in measuring the specific heats of salt solutions will serve both to emphasize the most obstinate difficulties in these measurements and to furnish the basis for a more intelligent criticism of the new methods to be described.

Person,* in 1851, made a few rather inaccurate determinations in this field. Later, Schüller † carried out a somewhat more extended series of measurements. Both these investigators used the simple method, which Andrews had devised in 1845, for the determination of the specific heats of liquids. A weighed amount of water was inclosed in a glass vessel, into which a thermometer fitted. This served as a "calorifer." It was heated to a given temperature, and then plunged into the solution and used as a stirrer. The temperature of the solution was measured at frequent intervals until it had become constant, or was regularly falling, and the procedure of Regnault employed to correct for the radiation of heat. The method of Andrews, as they employed it, had little to recommend it beyond simplicity. The correction for radiation was uncertain, while it is quite impossible for the thermometer in the calorifer accurately to measure its temperature.

Julius Thomsen ‡ was the first to make a protracted study of the specific heats of solutions. He pointed out the inaccuracies in the method just mentioned, and elaborated a very original method to overcome them. A known quantity of heat was furnished to the solutions by burning successively equal measured quantities of hydrogen in a platinum vessel, which they successively surrounded. Since the pressure of the hydrogen was kept accurately constant by an automatic device, the heating effect was directly proportional to the time, and therefore by choosing an initial temperature as much below the room temperature as the final was above it, no correction for radiation was necessary. The burning hydrogen is certainly superior to the calorifer of Person and Schüller; but the necessary apparatus is cumbrous, and the accuracy of the method is limited by the accuracy of the volumetric measurement of the hydrogen. The doubtful accuracy of the correction for radiation sets a further limit to the refinement of the method. In the skilled hands of Thomsen,

* Person, Ann. de Chim. et de Phys. (3), **33**, 437 (1851).

† Schüller, Pogg. Ann., **136**, 70 (1869).

‡ Thomsen, Thermochemische Untersuchungen (1882).

results were obtained which were concordant to within one to two-tenths of a per cent.

Almost simultaneously with Thomsen, Pfaundler* published measurements of the specific heat of sulphuric acid at various dilutions, and Marignac published an extensive series of measurements of the specific heats of salt solutions, duplicating most of Thomsen's, and including many others. Both of these investigators employed the method of Andrews, but in an improved form. They interposed a blank experiment upon water between every experiment upon an unknown solution. In this way they were able to correct, both for the heat exchange with the surroundings, and for the lag of the thermometer in the calorifer. The efficacy of the former correction is, as was recognized, dependent on the constancy of the external conditions. The published results of Marignac are means of a number of determinations, and for these he claims an accuracy of from one to two one-tenths of a per cent. They agree, on the average, with the measurements of Thomsen to within about two or three one-tenths of a per cent.

Pfaundler,† before this, had devised an electrical method for the measurement of the specific heats of liquids. Here a known amount of heat is furnished to the liquids by the conversion of electrical energy into heat. Two wires of the same resistance were prepared, and one coiled up in a calorimeter containing the liquid of unknown specific heat. These coils were arranged in series, and a current passed through them. The rise in temperature in the two liquids was of course inversely proportional to the heat capacity. If these capacities were nearly the same, the correction for radiation practically canceled out. If they differed widely, the resistances were so altered that the temperature rise was nearly the same with the same bulk of liquid.

For use with electrolytes, the heating coils must of course be insulated, and Pfaundler was unable to find a satisfactory coating for them. He finally‡ resorted to coiled glass capillaries containing mercury. The resistance of mercury, however, has so large a temperature-coefficient that he was obliged to measure the resistance of the coils at frequent intervals during a determination. His results were not especially accurate. In the few results which he published the error is at least as great as one one-tenth of a per cent, and this in spite of the fact that, by means of a delicate thermopile, which measured the difference between the

* Pfaundler, Sitzungsber. d. Akad. d. Wissen., Wien, **62-2**, 379 (1870).

† Pfaundler, Ibid. **59-2**, 145 (1869). ‡ Pfaundler, Ibid., **100-2a**, 352 (1891).

temperatures of the two solutions, he had reduced the thermometric error to a low value.

The method of Pfaundler has since been somewhat modified and used effectively by Magie, in whose hands it has attained very considerable accuracy.*

The method of Andrews, of Thomsen, of Marignac, and to a less extent the electrical method of Pfaundler and Magie, involve a more or less fortuitous correction for the heat exchange with the surrounding. All of them further involve the thermometric difficulty of accurately measuring a rapidly rising or falling temperature. Both these errors seem at first sight unavoidable in specific heat determinations. In 1887 Hesehus † attempted to avoid these difficulties by making the final temperature that of the surrounding air. This he accomplished in the following very simple fashion. After the hot body, whose specific heat was to be determined, had been brought into the calorimeter, he added cold water, little by little, at such a rate that the temperature in the calorimeter remained constant. Knowing the initial temperatures of the hot body, and the cold water, and the temperature in the calorimeter, and knowing the weight of the hot body and of the water added, he could evidently calculate the specific heat. Since there was no temperature change in the calorimeter, there was no heat exchange to correct for, and since the temperature of the hot body, the cold water, and the water in the calorimeter were stationary, the temperature measurements could be made under the most favorable conditions. Hesehus determined the specific heat of brass in this way, and Waterman,‡ after improving the technique of the method, made extended determinations of the specific heats of metals. His results showed excellent concordance (0.05 per cent) and established the efficacy of the method.

The method of Hesehus and Waterman is a great improvement over that of Andrews, because the final medium temperature at least is measured accurately. This medium temperature in specific heat determinations is of more importance than either the higher or the lower temperature, since an error in it is magnified in the calculation. Nevertheless, the cooling of the warm body just before the mixing, and the warming in transit of the cold water gradually added, bring in here also the old difficulty of the dissipation of heat in a new form.

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* W. F. Magie, Physical Review, **9**, 65 (1899); **13**, 91 (1901); **14**, 193 (1902); **17**, 105 (1903).

† Jour. de la Soc. Phys. Chem. Russ., Nov., 1887; Jour. de Physique, **7**, 489 (1888).

‡ Phys. Review, **4**, 161 (1896).

A New Method.

In devising a new method for determining the specific heats of liquids, the endeavor was made to retain the advantages of the method of Hesehus, while minimizing the disadvantages. The important objects to be accomplished were the following: —

First, the thermometers must all be read while stationary, not with a moving thread of mercury.

Secondly, as little time as possible must be allowed for the cooling of the hot liquid or the warming of the cold liquid.

Thirdly, conditions must be so adjusted that these two last-named errors, each made as small as possible, should cancel one another.

The first of these objects was attained by keeping both the hot and the cold liquids in very accurate thermostats before the moment of mixing, and by mixing them in a calorimeter surrounded by a thermostat maintained at the final temperature of the mixture. Thus all the temperatures were measured accurately, without the possibility of thermometric lag.

The second object was attained by delivering the two liquids into the mixing calorimeter simultaneously with great rapidity, having previously so adjusted their relative weights, and their relative temperatures, that their equilibrium temperature would be nearly identical with that in the water jacket of the calorimeter.

The third object was attained by making all the delivering apparatus as similar as possible in the two cases, and by having the temperature of the hot liquid as much above the final temperature as that of the cold liquid was below it.

The quickest adjustment of the final temperature is attained if the liquids are allowed actually to mix, not merely to equalize their temperatures through a heat-conducting septum. But if two liquids dissolve one another, they almost invariably evolve or absorb heat in the process. This extra heat adds algebraically to the heat-capacity effect, and must be subtracted in order to obtain this alone. Fortunately the heat of reaction is easily found in the present case by making additional experiments with the same apparatus, maintaining all the thermostats at the same temperature; or still more simply by means of another device described on page 675.

With these data, knowing the specific heat of one of the liquids within the given range, it is easy to calculate both the specific heat of the other liquid and that of the mixture, as will be shown.

The Hot Thermostat.

As has been said, the new method requires the two solutions should mix quickly and completely. To accomplish this, glass pipettes, each of about 0.23 liter capacity, were constructed to contain the liquids, and provided with ground-glass stoppers inside the lower ends of their bulbs, as illustrated below. These stoppers could be pulled out simultaneously by means of long silver wires. The entrance tubes were made of large enough bore to admit easily both the silver wires and large Beckmann thermometers. The exit tubes had bores of 10 mm. and therefore permitted a very rapid outflow of the liquids. These tubes were bent at such an angle that, when the pipettes were in place, the issuing streams met before striking the walls and floor of the receiving vessel in the calorimeter.

The method further required that the solutions in these pipettes should be kept at constant temperatures, one above, the other below, that of the room. The temperature of the solutions must be known to within the thousandth of a degree, and the development and construction of thermostats which would permit this was the main difficulty of the research.

Thermostats maintaining a temperature above that of the room, with the required constancy, have been constructed by Bradley,* Geer,† and others. In the present research, that of Bradley was chosen, as offering the fewest difficulties of construction. The action of the thermostat depends on the automatic regulation of an inflowing stream of hot water. This regulation is accomplished by the alternate contraction and expansion of a suitable liquid, inclosed in a long spiral tube, whereby a column of mercury is raised or lowered, and thus made to open or close the end of a capillary tube through which the warm water enters.

The thermostat, as used here, is partially illustrated in the diagram.‡ It differs in several respects from the instrument as described by Bradley.

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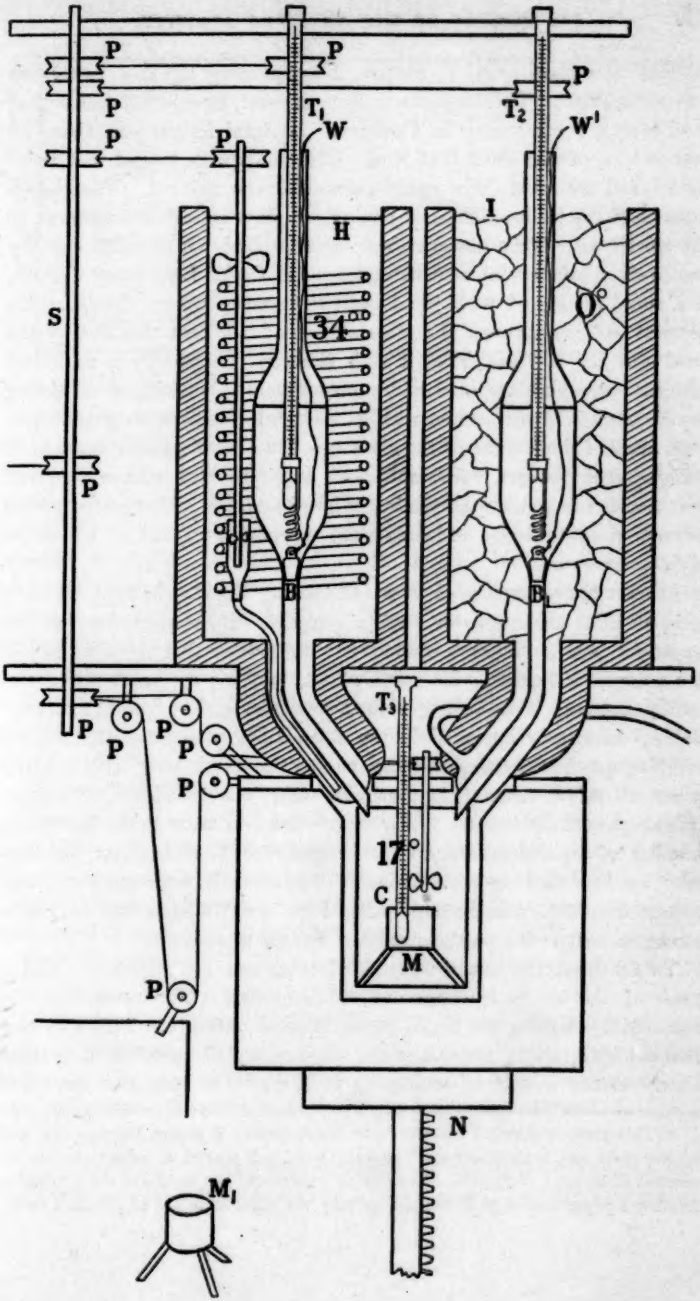
* Journ. Phys. Chem., **6**, p. 118 (1902).

† *Ibid.*, p. 85 (1902).

‡ The following designations will assist in the understanding of the diagram: —

B, B′. Stoppers in pipettes.
C. Calorimeter for mixing.
H. Hot thermostat.
I. Cold thermostat.
M. Platinum ring and tripod to prevent spattering.
M′. Perspective view of same, removed.
N. Vertically movable supporting stand for calorimeter.
P, P. Pulleys for driving stirrers.
S. Motor shafting.
T_1, T_2, T_3. Thermometers.
W, W_1. Wires for pulling stoppers (B, B′).


P
P
P
P
P
P
P
P
P
P
P
P
P
P
P
P
T_1
W
T_2
W'
H
I
S
34
0°
B
B
T_3
17°
C
M
N
M_1

In place of a glass spiral to contain the expanding liquid, a metal one was substituted. This was made from several lengths of thin-walled steel tubing, 1 centimetre in diameter. Its total length was about 30 feet and its volume about 0.45 litre. The joints were brazed and re-inforced, and the whole thoroughly galvanized and painted. The change introduced the inconvenience of joining the glass cut-off arrangement to the steel tube. This, however, was accomplished without difficulty, by means of a commercial cement called de Kotinsky Laboratory Cement. The spiral responded with great rapidity to temperature changes. To prevent leakage through the glass stopcock* we bent that end of the steel tube into a U and filled it with mercury. Evidently a much less efficient stopcook is required with mercury than if benzol (the expanding liquid) were in direct contact with it. Further, bulbs were provided in both arms of the U-tube of the glass cut-off, to afford greater latitude of temperature changes. An additional inlet provided with a stopcock was inserted to admit when desirable large amounts of hot water. This proved of convenience in heating the thermostat rapidly to about the right temperature.

Ether was first employed as an expanding liquid. In many respects it is an ideal substance for such a purpose. Its coefficient of cubical expansion and its relative conductivity are greater than those of any of the commoner liquids. Its specific heat, too, is very small. Unfortunately, not only is its boiling point inconveniently low, but, in standing, bubbles invariably appeared in the spiral tube, even when the method of filling precluded the possibility of any bubbles having been initially present. After many trials, therefore, ether was abandoned, in spite of its exceptional advantages. After ether there is little choice between a number of organic liquids, such as benzol, toluol, chloroform, and acetone, as the following table shows. The alcohols were quite unsuited to our use, for beside having rather high specific heats they exerted a strong solvent action on the cement. Benzol was chosen.

To fill the spiral, benzol was poured in at one end; by proper tilting most of the air was forced out at the other. The remainder was removed by boiling the liquid under reduced pressure. This was carried out by attaching the end of the spiral to a glass tube, which reached nearly to the bottom of a filtering flask, which in turn was connected

* This glass stopcock is not shown in the diagram; it was at the opposite end of the steel coil from the cut-off arrangement, and served to admit the proper amount of liquid to the spiral. In order to understand the details of the apparatus, Bradley's paper should be consulted, for only the differences are emphasized here.

Liquid.	Coefficient of Cubical Expansion.	Relative Conductivity ($H_2O = 1$).	Specific Heat
$(C_2H_5)_2O$	0.0021	0.33	0.40
C_6H_6	0.0014	0.22	0.36
$CHCl_3$	0.0014	0.29	0.35
$C_6H_5CH_3$	0.0014	. . .	0.43
$CaCl_2 + H_2O$ (46%)	0.00045	0.95	0.83

with a water pump. The pump was started and the liquid in the spiral kept boiling until most of it had boiled or been ejected over into the filter flask. The pump was then disconnected, and the liquid, free from air, was now pressed by the atmosphere back into the spiral. Enough liquid was always previously placed in the filter flask, so that at the end no air would go back with the liquid. This process was repeated several times at each end of the spiral. The bubbles were thus removed with such certainty that the opacity of the metal tube is not, as Bradley feared, a disadvantage.

The shape of the thermostat was of course governed by the shape and dimensions of the pipette. Further, it had to be provided with a protruding jacket or snout surrounding the lower tips of the pipette, else the temperature of the liquids would be altered in running out. The water in the thermostat was vigorously stirred by means of a small, but rapidly revolving, propeller. This did not have much effect on the water in the snout, and a second smaller propeller was attached to the same shaft and made to fit quite closely *inside* of a glass tube. From the end of this glass tube a rubber tube extended down to the very tip of the snout. This second propeller acted as a pump, and kept up a vigorous circulation of the water in the snout.

The hot water was furnished by a large copper thermostat heated by gas. Its temperature was kept constant by means of an ordinary Ostwald regulator at about 50°, that is, about 16° above that of the hot pipette-thermostat. A regulator is scarcely necessary, as large fluctuations in temperature seem to have no effect on the constancy of the hot thermostat. The water, as it left the heater, was filtered through a piece of fine silk cloth.

As long as the mercury and the glass cut-off were fairly clean, this thermostat proved admirably suited to the purpose. When equilibrium

had been established, often for hours at a time no change could be detected on a Beckmann thermometer which could easily be read to thousandths of a degree. In the latter part of the work the mercury occasionally caught in the annular space outside the capillary inlet tube, causing sudden and vexatious fluctuations of temperature. This would perhaps be obviated by a different ratio between the size of the capillary entrance tube, the size of the annular space, and the head of the water. It was found more convenient, however, to discard altogether the method of cutting off the flow of hot water directly by means of the mercury column, and to use the mercury as a means of making and breaking a feeble galvanic current. When made, this current actuated a relay which in turn sent a stronger current through an electro-magnetic arrangement for cutting off the supply of hot water. This apparatus worked admirably, and was used in a few of the last experiments.

The Cold Thermostat.

It was endeavored, at first, to maintain a constant temperature below that of the room, by passing a rapid stream of tap water around the pipette containing the solution. This gave surprising constancy at times, but was usually far too variable for the purpose. In the hope of increasing its constancy, the tap water was then made to pass first through a large mixing vessel, itself well insulated by an outside jacket of running water. This was a slight, but inadequate improvement. A special apparatus was therefore devised, but this apparatus was finally supplanted by a much simpler one, and therefore need not be described in detail. It utilized the tap water as a cooling agent, being available whenever this is tolerably constant, and consisted essentially of two water jackets, one inside the other, insulated from one another with cotton wool. The inner one contained the pipette, wherein the solutions were placed. The liquid within the pipette has been kept in this device for over an hour without suffering the slightest change in the temperature as observed by means of a very sensitive Beckmann thermometer.

As has been said, this method also was discarded for the much simpler one of packing the pipette in ice, — a proceeding which would have been adopted in the first place had it not at first seemed advisable to maintain a temperature somewhat above the freezing point. By using pure ice, mixed with previously chilled, boiled, distilled water, we were able to do away entirely with the measurement of the temperature of the cold solution, because it was exactly zero. This of course was a distinct gain.

Here as in the hot thermostat, the tip of the pipette had to be maintained at the same temperature as the bulb. The similar glass jacket or snout provided for this purpose could not be so well insulated as the body of the thermostat, and therefore was provided with an outlet tube by means of which ice-cold water could be run through it from above. Thirty seconds before the solution was run out from the pipette, this current of ice-cold water was started, and thus the tip of the pipette, already very cold, was brought to zero.

The Calorimeter and Remaining Apparatus.

The construction of a calorimeter in which the hot and cold liquid should mix presented no especial difficulty. The receiving vessel itself was a platinum can weighing some 100 grams, and having a capacity of 0.5 litre. This was supported on corks in a somewhat larger can of tinned iron, which in turn was sunk in a large jacket of water. It was found important to have the annular space between the two cans as small as possible, in order to make sure that the platinum can was at the same temperature as water in the jacket. To make this doubly sure the annular space was packed around the top with a little wool. The whole was covered with a tight-fitting wooden cover.

The liquids fell into the platinum can with considerable violence. This was necessary, if the pipettes were to be emptied in the brief space of a couple of seconds. Much difficulty was at first experienced in the spattering which thereby results, — an evil which was finally remedied by a very simple cylindrical device of platinum foil resting on the floor of the platinum can. It is pictured in the diagram. As a further security and to assist in preventing evaporation, a thin lacquered-iron cover and an outer wooden cover were fitted over the top of the platinum can. In order to shorten as much as possible the distance through which the liquids must pass while exposed to the air, two holes were provided in the covers of the calorimeter large enough to admit the snouts of the two thermostats. In this way the tips of the pipettes were brought directly into the platinum can, and the exposure of the jets was very slight. These holes, when not in use, were closed tightly with corks. It was further important that the ends of the snouts should not remain inside the calorimeter any longer than necessary, although the involved error would have been small, since one snout was as hot as the other was cold. In order to accomplish this easy removal, the calorimeter was placed on an adjustable stand, which by means of a rack and pinion could be raised and lowered with rapidity and certainty.

The liquids must evidently be stirred both before and after mixing. Because of the small available space in the entrance tubes of the thermostat-pipettes the thermometers were utilized for stirring the initial hot and cold liquids. For this purpose small spiral-shaped pieces of silver foil were attached to the lower end of the thermometers projecting somewhat below the bulb. The upper end of each thermometer was provided with a bearing from which it hung, and which permitted the thermometer to rotate about its long axis. A thin glass tube was snugly fitted over the shaft of each thermometer, and this, rubbing against the upper tube of the pipette, furnished the second bearing. The spiral-shaped piece of foil acted like a screw, and produced circulation of the liquids in the pipettes.

The stirring in the cold solution was discontinued as soon as the thermometer immersed in it showed that the constant temperature of zero had been reached. The mixed liquids in the platinum can were stirred by means of an inverted glass T-tube, provided with holes along its vertical arm, and rotating at a moderate speed. The belting which ran this was so arranged as not to interfere with the free vertical motion of the calorimeter (see diagram). A simple catch was also provided, such that a single motion sufficed to start or stop this stirrer.

Unfortunately a few drops of the liquid always fell from the pipettes after the main body of the liquids had rushed out. We could not be at all sure that these drops were at the same temperature as the rest of the liquid. For that reason an arm was constructed which carried two glass cups, and which could be swung beneath the ends of the pipettes the moment the calorimeter had been lowered.

For results accurate only to between 0.1 and 0.2 per cent, it would be possible to neglect both these drippings and the liquid remaining in the pipettes. For more accurate measurements, the amounts of these drainings and drippings must be determined. At first it was planned to weigh them, having collected the liquid left in the pipettes in suitable absorption tubes after evaporation by means of a current of dry air. This proved to be a very tedious process.

A much more expeditious and satisfactory method was finally adopted with water or aqueous solutions. Instead of dry air, the pipettes were rinsed with dry acetone, the drippings added to this, and the whole made up to 50 millilitres at 25°. The water in the mixture was then determined by means of specific gravity measurements, and was subtracted from the total weight of water originally in the pipettes in order to find the amount which actually found its way into the calorimeter.

For the specific-gravity determinations a thermostat was constructed which maintained a constant temperature of 25° within the one one-hundredth of a degree. It was heated by means of an incandescent electric-light bulb, and regulated by a simple regulator filled with alcohol and a little mercury, which, instead of cutting off a current of gas, made and broke an electric relay current, which in turn opened or closed the lighting circuit. A glass float was then made which was adjusted so that it neither sank nor floated in a known mixture of acetone and water containing a slightly greater percentage of water than was usually present in the unknown mixtures. After each mixture had remained an hour in the above thermostat the float was put in and water added from a burette until the float just sank. Acetone was then added until equilibrium was reached. Since the mixture to which the float was adjusted contained about 3 per cent of water, evidently the volume of the water needed to be known with much greater accuracy than that of acetone. The water burette was therefore very narrow, and was graduated to hundredths of a millilitre. The float was easily sensitive to less than one one-hundredth of a gram of water, and since the total amount of water usually amounted to somewhat more than 170 grams, the error in this method affected the final result by less than one one-hundredth of a per cent.

When the solutes in the solutions whose specific heats are being determined are insoluble in acetone, this method can be used for them also. This was the case with copper sulphate. If a given solute is soluble in acetone the pipettes can be rinsed with water, and the amount of the solute in this determined by chemical methods. This was the case with silver nitrate, for example.

Beckmann thermometers were used to measure the temperature of the hot liquid, the cold liquid, and the mixture. The scales were all divided into one-hundredths of a degree, and by means of a small lens could be read to within a one-thousandth of a degree with certainty. A set of Baudin thermometers, described elsewhere, was used to standardize these.* Comparisons were made in all cases under experimental conditions, and the zero point of the standard was afterwards taken.

The apparatus having been described, it is desirable to emphasize its advantages.

In the first place, all error from thermometric lag is avoided. Again, such slight errors from cooling as may be present during transference is compensated by an equal and contrary heating effect, for while the liquids

* Richards, Am. Jour. Sci. (4), 6, 201 (1898).

are falling from the ends of the pipettes into the mixing vessel, the absorption of heat from the surroundings, by the cold liquid, exactly cancels the radiation of heat from the warm liquid. Even the cooling and warming due to evaporation and condensation are also practically identical, since the air through which the liquids pass is saturated with water vapor. It will be seen, in the description of the apparatus, that not only do these errors cancel, but the errors themselves have been almost eliminated, by making it possible to raise the calorimeter, just before the liquids are to run out, to such a height that the tips of the pipettes are within the calorimeter.

The possibility of an unequal radiation or absorption of heat by the two liquids after transference must however be considered. Such a thing could happen only if the mixing was tardy, — for example, if the cold solution chanced to remain for some time close to the walls of the mixing vessel, while the warm water, for the most part, occupied a more central position. The following consideration will show how remote such a contingency must be. In the first place, the stoppers, which released the liquids, were pulled out within $\frac{1}{3}$ to $\frac{1}{5}$ of a second of one another. The exit tubes were identical in form and length, and were so directed that the two issuing streams met before striking the walls and floor of the mixing vessel. Further, the very moment that all the liquid had run out (and this required only about two seconds), active stirring of the mixed liquids was begun. In less than 90 seconds more, the precise final temperature was established, It is evident that the great difference of temperature must have been equalized within a very few seconds after mixing. We have seen, then, that not only is an unsymmetrical distribution of the hot and cold liquids unlikely, but if this should occur its duration must be exceedingly brief.

Because the errors due to radiation after, before, and during mixing were thus eliminated, it is evident that the accuracy of this method must depend first, on the accuracy with which the relative amounts of the two liquids are known, and second, on the refinement of the temperature measurements. The initial weights of the two liquids can be known with all the desired accuracy. By taking care to avoid evaporation and by determining the amounts of liquids left in the tubes, we can be almost equally sure regarding the amounts of the liquids which actually mix. It appears, then, that the accuracy of the method must depend chiefly on the refinement of the temperature measurements.

Of the temperature measurements, that of the *mixture* is the most important; because an error in it has the greatest effect on the final

result. The reason for this is, that we determine the fall in temperature of the warm liquid by subtracting this equilibrium temperature of the mixture from the initial temperature of the warm liquid; while we also determine the rise in temperature of the cold liquid by subtracting its initial temperature from the temperature of the mixture. Any error, then, in this latter temperature measurement has a double effect on the specific heat.

The accuracy of the thermometry, of course, depends primarily on the thermometers employed. It will suffice to say here, that, by comparing the thermometers with standards after every experiment, and taking the zero point of these latter, and making the correction when necessary for exposed thread and hydrostatic pressure, we have usually felt sure of the equilibrium temperature to within two or three one-thousandths of a degree. This, with the usual fall of temperature of 17 degrees, would correspond to a percentage error of $\frac{2 \times .0025}{17.000}$, or about 0.03 per cent.

The stationary condition of the thermometer is so favorable to precise measurement of temperature that it seems by no means impossible that, using still greater precautions in the temperature measurements, by means of platinum resistance thermometers, one might be sure of the temperature of the mixture to within less than a single one-thousandth of a degree, which, with the same temperature fall of seventeen degrees, would correspond to an uncertainty in the specific heat of less than 0.01 per cent. This would far exceed the accuracy with which the varying specific heats of water are now known.

As we have just implied, the accuracy of the method is directly proportional to the temperature fall of the warm liquid, or the temperature rise of the cold one. But the specific heat which is measured is the *mean* specific heat over the temperature interval employed, and since we cannot be sure that the change of the specific heat with the temperature is linear, it follows that the greater the temperature interval, the less the certainty with which the specific heat at any given temperature is known. The temperature interval here employed was about seventeen degrees.

The rise in temperature due to the work done by the actual fall of the liquids from the pipettes can be easily calculated. Thus, the total weight of the falling liquids was about 350 grams; the length of the fall about 40 cm. The kinetic energy converted into heat, therefore, amounted to $40 \times 350 \times 981$, or 13,700,000 ergs, which corresponds very nearly to one-third of a calorie. This would have heated the 350 grams of mixture

nearly a one-thousandth of a degree. Further, the stirring of the mixture, though lasting for only a minute, must have exerted a warming effect. This also was found to amount to about one one-thousandth of a degree.

These two constant effects, the further possibility of the cold liquid not being exactly at zero degrees, constant thermometric errors, and other hiddden errors, were completely eliminated by making parallel determinations, using water in each pipette. Had it not been for these small constant errors, we should of course have obtained relative specific heats of the hot and cold water whose ratio corresponded to the ratio of the known mean specific heats of water between these temperatures, provided, that is, that the known value also is free from such errors. As a matter of fact, we found that these ratios were not exactly equal, but that they differed by a small constant amount, — less than 0.05 per cent.* The small magnitude of this difference is equivalent to proof that the apparatus just described gives about the same relation between the specific heats of the warm and cold water as has the work of others, and forms an excellent test of the efficiency of the present apparatus.

The computation with water in both pipettes is very simple; but, as has been said, the simple heat capacity of a solution is not determined by this method, for the heat of dilution is superposed when the cold solution is mixed with warm water. It is necessary, therefore, to make a separate measurement of the heat of dilution. In spite of the ease with which this latter measurement can be made, this might, under some conditions, be considered a drawback, and for that reason it was originally planned to have the liquids equalize their temperature without uniting. For this purpose there was devised a cylindrical vessel divided into two compartments by means of a thin, greatly convoluted partition. Since in the present work the heat of dilution was also of interest and value, as will be shown, the determination of the heat of dilution at this time involved no extra labor. For this reason the specific heats of solutions were determined by actual mixing, and corrected for the heat of dilution.

In passing, it may be noted that this apparatus could be used for determining the heat of reaction of solutions upon one another, when thermometric lag is to be excluded. One of the solutions could be placed in the calorimeter at the temperature of the room, and the other in one of

* The standard of comparison was the table chosen by Ostwald and Luther as representing the true values (Phys. Chem. Mess., p 195 [1902]). Our value for the ratio, 1 : 1.0059, was between the value derived from this table and the lower value to be derived from the work of Callendar and Barnes (Zeitschr. phys. Chem., **32**, 161 [1900]).

the thermostat-pipettes at a temperature just low enough to counterbalance the heat of the reaction, so that the mixture also would be at the temperature of the room. This application of the device will be tried in the near future.

The Heat of Dilution.

For the determination of the heat of dilution the same apparatus could have been used, adjusting all the thermostats to the same temperature. It was, however, much more convenient to use for this purpose a simpler and probably more accurate device, described below.

This device consisted merely of a beaker divided into equal right and left-hand compartments, by means of a detachable partition of silver foil. The partition was held in place by a narrow U-shaped ledge of glass cemented to the walls and floor of the beaker. To this ledge the silver foil was fastened, water-tight, by means of hard paraffine. A glass rod was securely attached by wires and cement to the partition, and by its means the partition could be easily detached from its supports. Water was placed in one compartment and the solution in the other. Each was provided with a stirrer and a sensitive Beckmann thermometer. The whole was then placed in a calorimeter at the desired temperature. As a rule, it was more expeditious to adjust the temperature of the liquids on either side of the partition to within a few one-hundredths of a degree of each other, before they were placed in the calorimeter. When the liquids in each compartment had reached practically the same temperature and were either stationary or very slowly rising in temperature, readings were made of the thermometers at the minute intervals. At a given moment, having made a final reading of the thermometers, the partition was removed, active stirring continued, and the thermometers read at intervals of a minute, until the same regular rate of warming or cooling had established itself. This seldom required more than two or three minutes. It was not difficult to make the necessary corrections for radiation over so short an interval. The *average* change recorded in both thermometers evidently represents the actual temperature change — since both liquids were not usually at exactly the same temperature.

Since the heat of dilution of these concentrations only amounts to a few one-thousandths of a degree, there is evidently no need of great accuracy in determining the quantity of liquids used. We therefore measured out equal volumes, using a pipette of 0.173 litre capacity. This reproduced very nearly the actual weights of water and solution used in the above determinations of specific heats. The heat capacity of the beaker

amounted to $110 \times 0.2 = 22$, or 92 mayers; about one-sixteenth of the total heat capacity of the mixture. In most cases this was negligible.

This simple apparatus is so efficient in its operation as to be worthy of use also in other thermochemical operations where great accuracy and small range of temperature is needed. The method in which the mixing is accomplished is certainly preferable to any method which demands the pouring of one of the liquids from one vessel into another.

Results.

A few actual results with the apparatus may now be discussed in order to show the accuracy which has been obtained. It is possible to calculate the specific heat of a solution by mixing water in this apparatus in two ways. The value for the solution over the range 0° to 17° may be based either upon the heat communicated to it by the warm water as calculated from the average specific heat of the warm water, and its fall of temperature in mixing, or else upon the value for water between 0° and 17° as found by mixing this cold water with exactly the same amount of hot water in parallel experiments. The two methods of calculating give almost the same value, the difference being less than 0.05 per cent, as was implied in previous statements concerning the quantitative mixing of hot and cold water made on page 674.

The cause of such slight difference as exists need not be at present discussed — it is enough to emphasize again the fact that reference of the cold solution to cold water measured in parallel experiments over the same range of temperature is by far the best, since thereby any possible constant errors of experimentation are eliminated, being canceled by appearing in each series. The results below with cupric sulphate and argentic nitrate are computed in this way. The heats of dilution were subtracted before the calculations were made. The calculations for the concentration $CuSO_4 + 200H_2O$ were made on the assumption that very slight dilution evolves only a negligible quantity of heat, which was shown to be true.

The "probable error" of this result, computed by the method of least squares, is only about 0.01 per cent. Constant errors must have been eliminated by the method of determination which compared the solution with water under exactly the same conditions, in parallel experiments. Hence the result is probably not far from the truth, although the series is claimed to be only preliminary, made to demonstrate the practicability of the method. Because there are no other determinations of such a solution between 0° and 17°, comparison with others is impossible. By

SPECIFIC HEAT OF CUPRIC SULPHATE SOLUTIONS BETWEEN 0° AND 17°.

Actual Composition of Solution.	Specific Heat compared with Water over the same Range.	Specific Heat of $CuSO_4 + 200H_2O$ (calculated).
$CuSO_4 + 216\ H_2O$	0.9469	0.9430
"	0.9469	0.9430
$CuSO_4 + 201.6\ H_2O$	0.9444	0.9440
"	0.9438	0.9434
"	0.9434	0.9430
		0.9433

extrapolating linearly the results of Marignac between 18° and 52° a result of 0.949 instead of the value 0.943 may be obtained, but this extrapolation is too uncertain to form a satisfactory basis of comparison.

In the same way, allowing for the heat of dilution, the specific heat of a solution $AgNO_3 + 196.7\,H_2O$ was found to be 0.9476. This has never been determined before at any temperature.

As has been said, the heat of dilution was found before calculating the above results. The results were as follows:

The rise of temperature on dilution of the cupric sulphate solution with an equal volume of water was found, in two experiments at 17° with the divided beaker-calorimeter, to be +0.008° and +0.010°, or +0.009° in average. This is then a warming effect.

The rise of temperature on dilution of the argentic nitrate was found in the same way, in three experiments to be at 16° −0.007°, −0.005°, and −0.006°; or −0.006° in average. This is a cooling effect, which was duly subtracted from the final temperature of mixing in the specific heat experiments.

In these determinations the purity of the salts is not of paramount importance, for the specific heats of the impurities would differ but slightly from that of the pure salt; nevertheless, pains was taken to secure high purity. An accurate knowledge of the concentration of the solution is of more importance, and the solutions were all carefully analyzed. Even this, however, does not require the greatest refinement for the specific heats of the solution are so nearly equal at this dilution to that of water that they change but slightly with changing concentration.

An Indirect Method of Measuring the Specific Heats of more Dilute Solutions.

Having once determined accurately the specific heat of a given solution, it is easy without much more labor to determine that of any more dilute solution of the same substance. The method for accomplishing this purpose, depending upon the change of the heat of dilution with temperature, was first suggested by Berthelot,* but seems never to have been used in actual practice. Probably the reason for this neglect was the difficulty of determining accurately with any ordinary apparatus the very small heats of dilution involved — but this difficulty is now removed by the very simple and convenient divided beaker-calorimeter, described above. Therefore it seems worth while to explain the method and report a few experiments demonstrating its value.

In principle, this method depends upon the well-known thermodynamic relation usually known as Kirchhoff's law, namely

$$K_1 - K = \frac{U_T - U_{T+t}}{t},$$

where K and K_1 represent heat capacities of factors and products respectively, and U_T and U_{T+t} heats of reaction (in this case of dilution) at the temperatures T and $T + t$. Having measured U_T and U_{T+t} by means of our apparatus, the change of heat capacity of the system during the reaction is very simply obtained; and if the heat capacity of the concentrated solution and the water are both known at first, the heat capacity of the more dilute solution is at once found. The dilute solution can then be once more diluted, and so on indefinitely.

This is a very accurate process, the error being divided instead of being multiplied in the operation.

The heat of dilution of the solutions at 16° or 17° had already been determined. Lack of time and the high temperature of summer weather (June, 1904) prevented us from carrying out the dilution of one of the previous solutions at 0° as would have been desirable, — for $t°$ should cover the range over which the specific heats have been studied. Nevertheless, a few determinations of the heat of dilution of the argentic nitrate made at 24° will show the mode of applying the problem and afford a fairly accurate result. In four experiments, the temperature-changes on the dilution of the argentic nitrate solution, with an equal bulk of water

* Mech. Chim., I, p. 278 (1879).

at 24°, were respectively −0.002, −0.005, −0.006, −0.006; or on the average $-0.005 = U_{T+t}$. At 16° this had previously been found to be $-0.006 = U_T$. Then $K_1 - K = \frac{(-0.006° + 0.005°)\,7060}{8°} = -0.9$.

The total heat capacity having been in the first place $0.9476\ (170 + 196.7 \times 18) + 196.7 \times 18 = 7056.8$ (that is, the sum of the separate heat capacities of the argentic nitrate solution and the water) the heat capacity of the mixture will be $7056.8 - 0.9 = 7055.9$, and the specific heat will be this quantity divided by the heat capacity of an equal weight of water, or $(170 + 196.7 \times 18) + 196.7 \times 18 = 7251.2$.* The specific heat of the dilute solution is thus 0.9731.

Further determinations of many substances by all these methods will soon be made in this Laboratory. The determinations above given are only preliminary, as has been said; and they are recorded here rather to indicate the working of the methods under consideration than to fix the values in question. Much more accurate work could undoubtedly be done with the method if more pains was taken with the thermometry, without question the least certain of the measurements involved.

We take pleasure in acknowledging our indebtedness to the Rumford Fund of the American Academy of Arts and Sciences for generous pecuniary help in the construction of the somewhat complicated apparatus.

Summary.

1. A new method of determining the specific heat of solutions is described.

2. A new device for determining accurately the heat of dilution of a solution is described.

3. Both these methods involve only the reading of stationary thermometers, and therefore avoid error from thermometric lag.

4. In both methods error from uncompensated cooling is avoided as much as possible.

5. Each of these methods may be used for certain types of chemical reaction, as well as for the physico-chemical measurements above mentioned.

6. The method proposed by Berthelot for determining from the change

* It will be easily seen that the rounded-off values of the atomic weights suffice in this calculation, if a result no nearer than 0.01 per cent is needed.

of the heat of dilution with temperature the specific heats of increasingly dilute solutions is tested for the first time.

7. Several devices and methods of experimentation are suggested and tested; especially a simple method for determining the water adhering to glass vessels, and the construction of a very sensitive thermostat.